COAGULATION AND FILTRATION OF SOLIDS FROM LIQUEFIED COAL OF SYNTHOIL PROCESS

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Introduction

The idea of improving the separation of solids from coal liquefaction product by dilution with a solvent or coagulation with an antisolvent is not new. The literature on the subject is reviewed in a recent report (1)[4]. A patent dated 1970 suggested using a solvent such as acetone, or aromatic or aliphatic hydrocarbons (2). An earlier patent suggested adding a paraffinic liquid (antisolvent) to precipitate benzene insolubles and asphaltenes (3). A 1972 patent described the agglomeration of solids by recycling a fraction of the coal liquefaction product (4). A 1974 patent, assigned to The Lummus Company, emphasized the use of an antisolvent with paraffinic characteristics (5). Additional information on the agglomeration and separation of solids by the Lummus process was presented in 1975 (6). Separation of the agglomerated solids is conducted by gravity settling. Deasphalting of coal extract with saturated hydrocarbons is described in (7).

The purpose of the present investigation was to coagulate the solids in liquefied coal from the SYNTHOIL process with a process-generated antisolvent and to remove the agglomerated solids by filtration rather than settling. In the SYNTHOIL process for converting coal to a nonpolluting utility fuel oil, coal is liquefied and hydrodesulfurized catalytically by reaction with hydrogen in a turbulent-flow, packed-bed reactor (8). The gross liquid product is then centrifuged, or filtered, to remove the minor amounts of residual unreacted coal and mineral matter. If a method for agglomerating the finely divided solids in the gross liquid product could be developed, the subsequent separation of solids will be easier and more complete. Such a method and the experimental data in support of it are described below. It is not yet possible to comment on the economics of the method.

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Method

The method for agglomerating and separating the solids present in the gross liquid product consists of the following steps:

(1) Prepare a blend of the gross liquid product with an accumulation of light oil derived from the SYNTHOIL process (9). The blend may contain 40 to 50 weight per cent of the gross liquid product.

(2) Hold the blend at 105° - 115°C for 10 minutes in a vessel fitted with a reflux condenser.

(3) Filter.

(4) Wash the filter cake with the same light oil as used for preparing the blend.

(5) Recover light oil from the filtrate by distillation.

In the experiments described below, product oils containing less than 0.1 per cent ash were obtained by the method and the residual oil in the solids appeared to be negligible.

Materials and Experimental Procedure

Analyses of the gross liquid product and the light oil used in this work are given in tables 1 and 2, respectively. Although not evident from the analysis, the light oil had an ammonia odor. Using a Waring blender, mixtures of the gross liquid product and the light oil were prepared by the following techniques:

1. The components were blended for 5 minutes during which time the frictional heat raised the temperature of the mixture to 60°C.

2. The components were blended for 15 minutes during which time the mixture boiled due to the frictional heat.

3. A mixture of 80 parts by weight of the gross liquid product and 20 parts by weight of the light oil was blended for 5 minutes and then diluted to mixtures containing 10 to 50 per cent by weight of gross liquid product by shaking with calculated quantities of the light oil.

4. The diluted mixtures prepared in 3 were refluxed for 10 minutes, at 105° - 115°C.

The mixtures prepared in 1 to 4 were cooled to room temperature for filtration tests and viscosity and density determinations.

The filtration equipment, shown in figure 1, consisted of an 8 inch length of 1-3/8 inch ID steel pipe fitted with a screwed top gas and thermocouple adapter and a bottom filter assembly. The latter comprised a paper disc clamped between a 1.3 inch ID Teflon ring and a disc of 62 x 62 per inch square weave gauze on a perforated brass disc. The filter assembly was tightened with a wrench but the top assembly was only hand-tightened, enabling it to be rapidly opened, refilled, and screwed tight. The filter was clamped above a beaker mounted on a triple beam scale. For filtration rate determinations, mixtures were poured into the tube, the top assembly fitted, a constant nitrogen pressure of 25 psig applied, and the time intervals for collecting known quantities of the filtrate noted. With dilute mixtures, it was necessary to build-up filter cake to reduce the filtration rate before rate measurements could be made. Specific resistances of filter cakes were calculated by the method described by McCabe and Smith (10).

The viscosities of the mixtures and filtrates were measured on 8 ml samples with a Brookfield Synchro-Lectric model LVT viscometer in a Thermosel constant temperature unit. The spindle model was SC4 -18. The measurements were conducted at room temperature and at a high shear rate of 79.2 sec^{-1} at 60 rpm. A series of viscosity determinations on the gross liquid product over a range of shear rates at three different temperatures had shown that the apparent viscosity is very sensitive to shear rate at low values of the latter (figure 2).

Results

The filtration rates are given as plots of reciprocal filtration rate, $\Delta t/\Delta v$, against average filtrate volume, $\bar{v}$, in figures 3, 4, and 5. Specific cake resistances calculated from the slopes of the graphs in figure 5 are given in table 3. The filtrates obtained from the experiments shown in figure 5 were analyzed for ash, organic benzene insolubles, asphaltene, and pentane-soluble oil and the concentrations of these components in light oil-free SYNTHOIL product were calculated by allowing for the known quantity of light oil in the filtrate. The calculated analysis of the recovered SYNTHOIL product is given in table 4. The viscosities of mixtures of gross liquid product and light oil, refluxed for 10 minutes, and of the filtrates obtained from them are given in table 5 and plotted logarithmically against log light oil fraction in figure 6.

Discussion

Generally, the results suggest that the gross liquid product contains fine solids that block the capillaries of filter cakes and prevent rapid filtration. The solids are agglomerated by thermal treatment with light oil and cooling to room temperature. High concentrations of light oil give very open filter cakes capable of extremely rapid filtration rates. Addition of light oil also reduces the viscosities of the gross liquid products and filtrates.

Figure 3 shows that a 50 per cent mixture of gross liquid product in light oil prepared without sufficient heating was slow to filter. A marked improvement in filtration rate was obtained by refluxing the slurry for 10 minutes, where a specific cake resistance of 3×10^{11} ft/lb (2 technical units) was found. Figure

4 shows similar effects with a 20 per cent mixture of gross liquid product in light oil. Blending for 5 minutes gave a cake resistance little different from that of the shaken mixture. Blending for 15 minutes showed a marked improvement but not as great as that obtained by refluxing the mixture for 10 minutes, where a specific cake resistance of 0.1×10^{11} ft/lb (0.06 technical units) was attained.

Comparison of the reciprocal filtration rates of 50 per cent to 20 per cent mixtures of gross liquid product in light oil, as seen in figure 5, highlights the marked dependence of the filtration rate of refluxed mixtures on concentration. The filtration rate of the 10 per cent mixture was too rapid to measure and that of the 60 per cent mixtures was very slow. The specific cake resistances found in these tests and given in table 3 tend to a lower limit of 0.1×10^{11} ft/lb (0.06 technical units) at 30 per cent gross liquid product and less. The curvature of the plots for the 50 per cent and 40 per cent gross liquid product concentrations shows that, inspite of agglomeration by thermal treatment, capillary blockage did occur. Once capillaries blocked, they could not be opened by washing.

The results in table 4 show that the concentration of organic benzene insolubles in the recovered SYNTHOIL product is also markedly reduced hy thermal treatment with light oil followed by filtration. The odd breakpoint in the plots of log viscosity versus log concentration of gross liquid product in mixtures shown in figure 6 could be due to precipitation of the organic benzene insolubles and larger asphaltene molecules (macromolecules) normally soluble in the products of coal liquefaction. The breakpoint occurs at about 30 per cent to 40 per cent gross liquid product concentration where there is a sharp decrease in organic benzene insolubles in the recovered SYNTHOIL product.

It should be noted that no solid filter-aids were added in these tests, the agglomerated solids acting as their own filter medium. From the electron micrographs in plates 1 and 2, the agglomerates appear to be chain-like. Many fine particles are also clearly visible.

The agglomerating action, or the antisolvent characteristics, of the light oil may be due to the saturates in it. As given in table 2, mass spectrometric analysis of the light oil showed it contained 44 per cent of C_5 to C_{16} saturates.

Conclusions

(1) The finely divided solids in the gross liquid product from the SYNTHOIL process are coagulated by heating a mixture of the gross liquid product and a process-derived light oil at 105° - 115°C for 10 minutes.

(2) The coagulated solids are amenable to rapid separation by filtration after the mixture is cooled.

(3) The concentration of ash in the product oil is not sensitive to the concentration of the gross liquid product in the mixture (see table 4).

(4) The filtration rate of a mixture is sensitive to the concentration of the gross liquid product in it (see table 3). The filtration rate of a mixture containing 60 per cent gross liquid product was too slow for practical purposes. The mixture must contain a minimum of 50 per cent light oil for adequate rate of filtration.

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Table 1

Solvent Analysis of the Gross Liquid Product

	Weight per cent
Organic benzene insolubles	8.1
Asphaltene[1]	26.3
Oil[2]	61.0
Ash	4.6

1 Asphaltene is soluble in benzene but insoluble in pentane.

2 Oil is soluble both in benzene and pentane.

Table 2

Analysis of Light Oil

ASTM distillation D-158

Volume per cent distilled	Temperature, °C	Volume per cent distilled	Temperature, °C
F.D.	78.0	60	169.0
5	104.5	70	179.5
10	113.5	80	193.0
20	124.0	90	213.0
30	134.5	95	229.0
40	146.5	End point	232.0
50	158.0		

Recovery: 96 per cent
Residue: 3 per cent
Loss: 1 per cent

Mass spectrometric analysis

Component	Weight per cent
Saturates, C_5 - C_{16}	44.0
Benzenes	21.3
Indanols and benzothiophenes	0.2
Phenols	7.9
Dihydrophenols, resorcinols, and thiophenols	7.1
Acenaphthenes and biphenyls	0.5
Naphthalenes	4.5
Indenes	1.6
Indans and tetralins	12.7
Total:	99.8

Table 3

Specific Resistances of Filter Cakes from Mixtures of Gross Liquid Products and Light Oil Refluxed for 10 Minutes

Gross liquid product in mixture, weight per cent	Specific cake resistance	
	$ft/lb \times 10^{11}$	Technical units
10	1/	1/
20	0.1	0.06
30	0.1	0.07
40	0.5	0.3
50	3.2	2.0
60	2/	2/

1/ Filtration rate was too rapid for rate measurement.

2/ Filtration rate was too slow for rate measurement.

Table 4

Analysis of Light Oil-Free SYNTHOIL Product Recovered from Filtrate

(Calculated from analyses of the filtrates and the known quantities of light oil in them).

*Gross liquid product in mixture, weight per cent	Analysis of Recovered Synthoil Product			
	Ash	Organic Benzene insolubles	Asphaltene	Oil
10	0.03	0.2	27.0	72.8
20	<0.02	0.4	24.3	75.3
30	0.04	0.4	26.8	72.8
40	0.05	1.4	29.5	69.1
50	0.01	2.5	31.3	66.2

* The mixtures were refluxed for 10 minutes.

Table 5

Viscosity of Mixtures and Filtrates
(Mixtures refluxed for 10 minutes)

Gross liquid product in mixtures, weight per cent	Viscosity of mixture, cp	Viscosity of filtrate, cp
0 (neat light oil)	-	1.6
10	2.5	1.8
20	3.4	2.2
30	4.6	3.0
40	8.6	5.1
50	27	13
60	129	65
70	800	N. D.*
80	4,090	N. D.*

* N. D. = Not determined

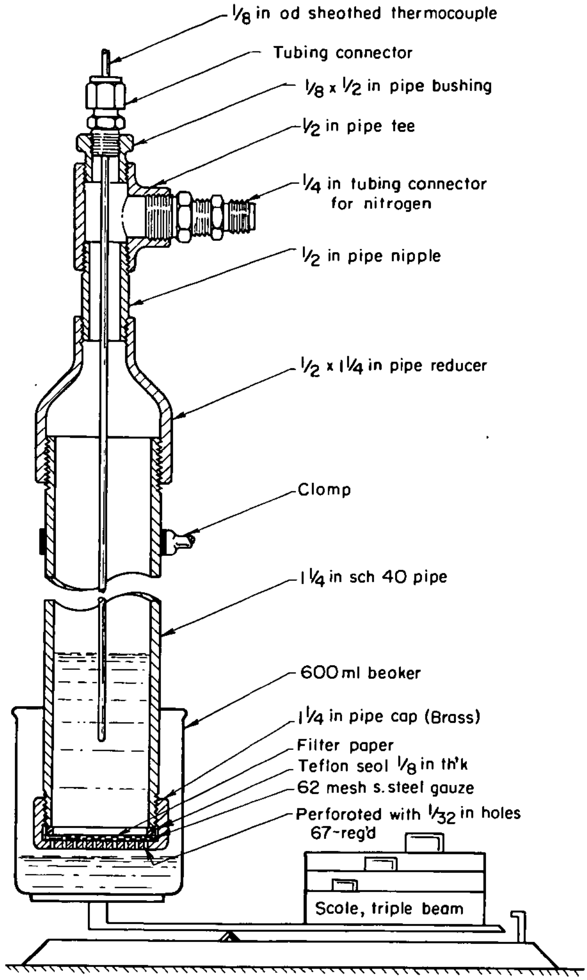

Figure 1.- Apparatus to measure filtration rates.

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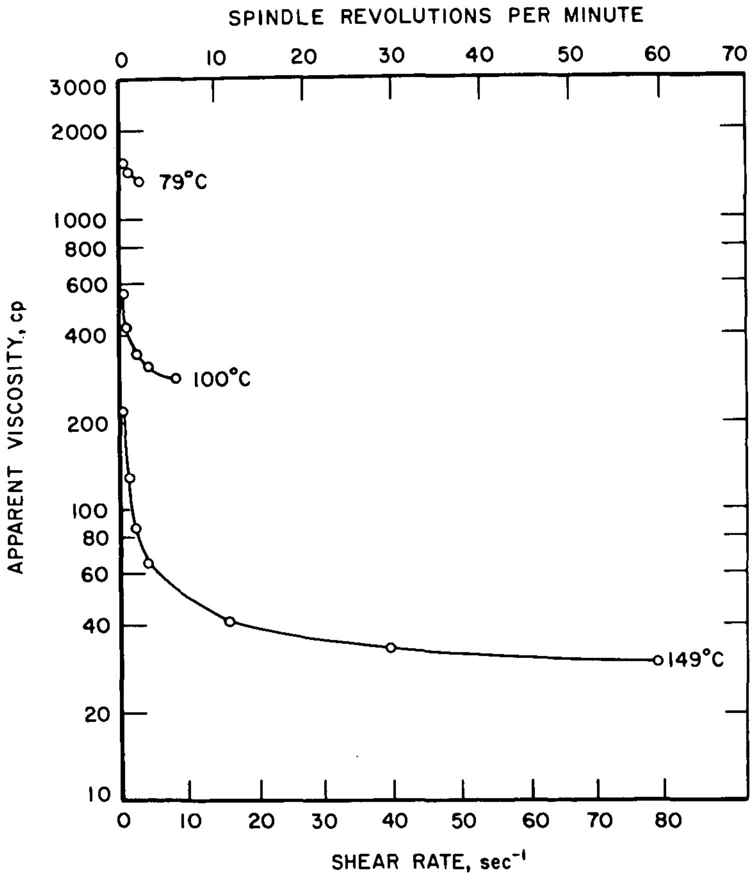

Figure 2–The effect of shear rate on apparent viscosity of gross liquid product.

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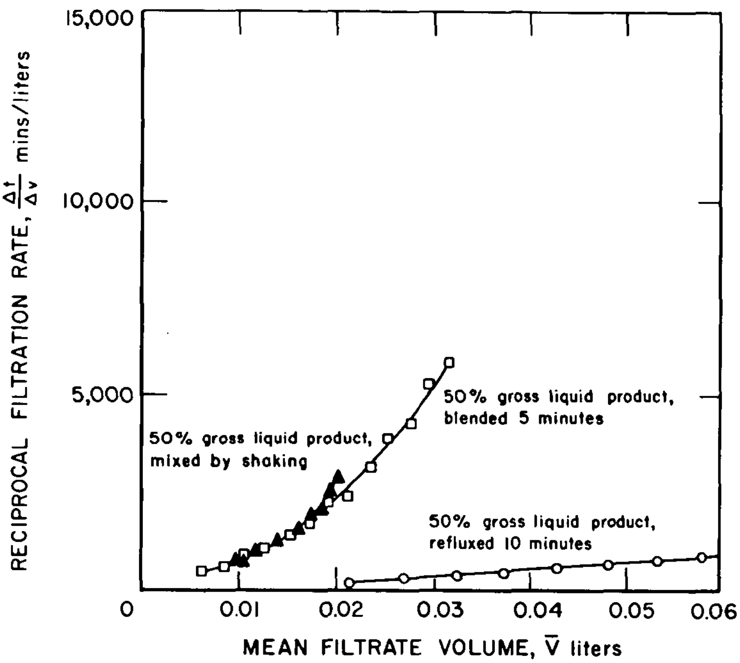

Figure 3– Dependence of reciprocal filtration rate on mixture treatment, (50% gross liquid product, 50% light oil).

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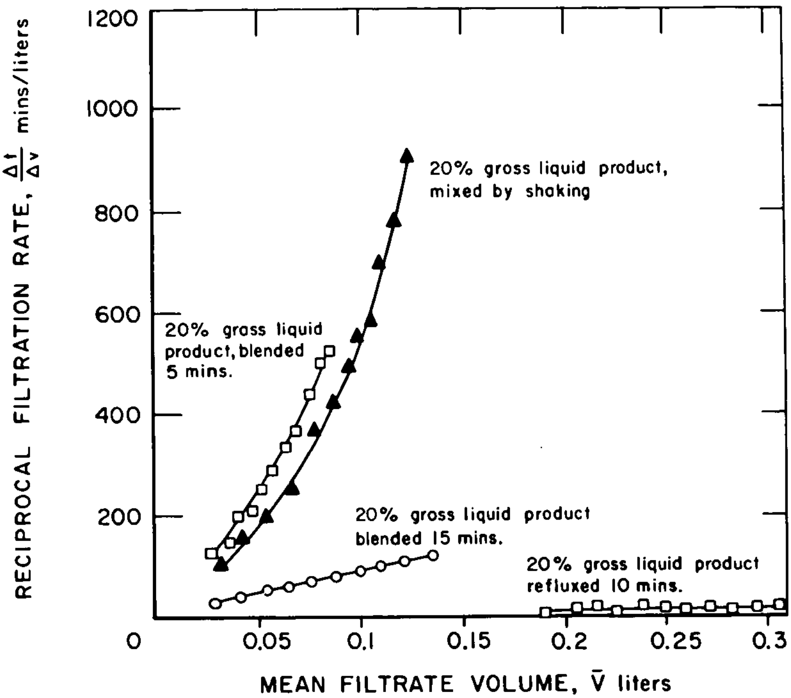

Figure 4 – Dependence of reciprocal filtration rate on mixture treatment, (20% gross liquid product, 80% light oil).

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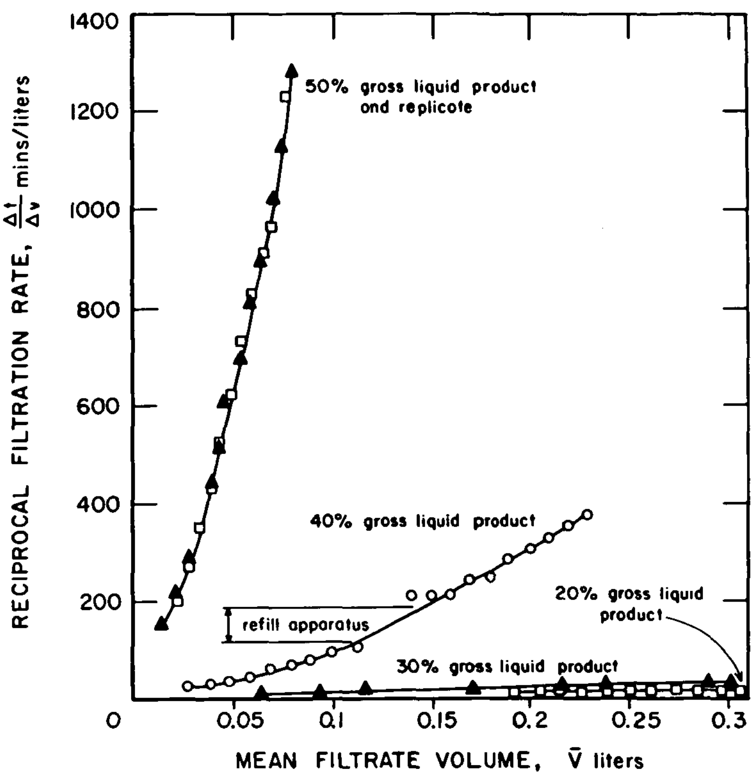

Figure 5–Dependence of reciprocal filtration rate on gross liquid product concentration in light oil (refluxed).

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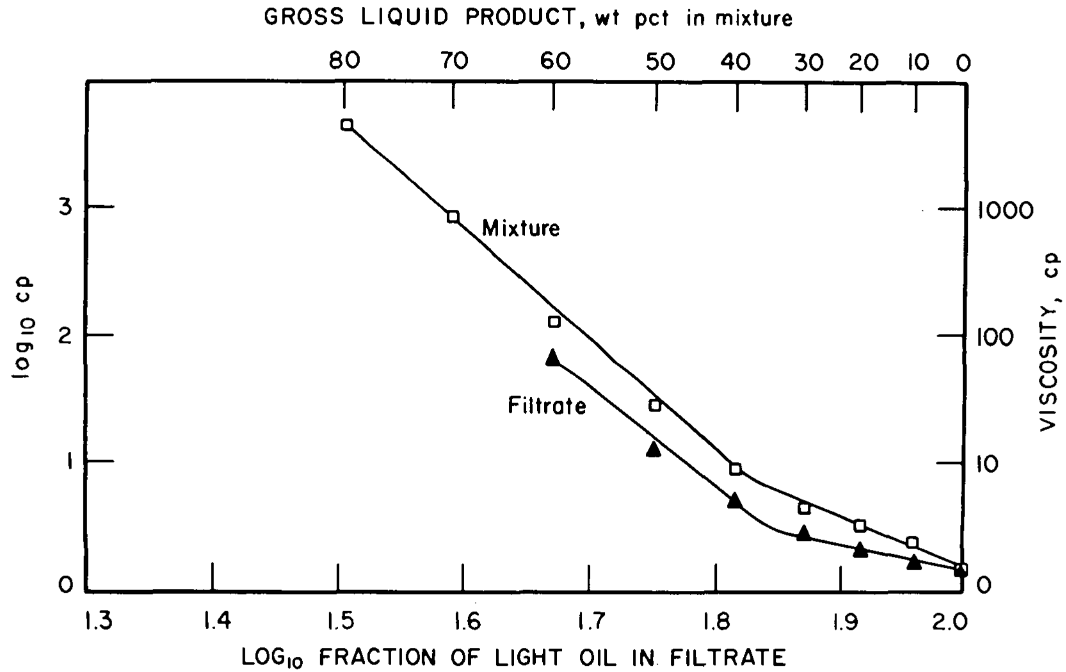

Figure 6–The effect of light oil concentration on viscosity of mixture and filtrate.

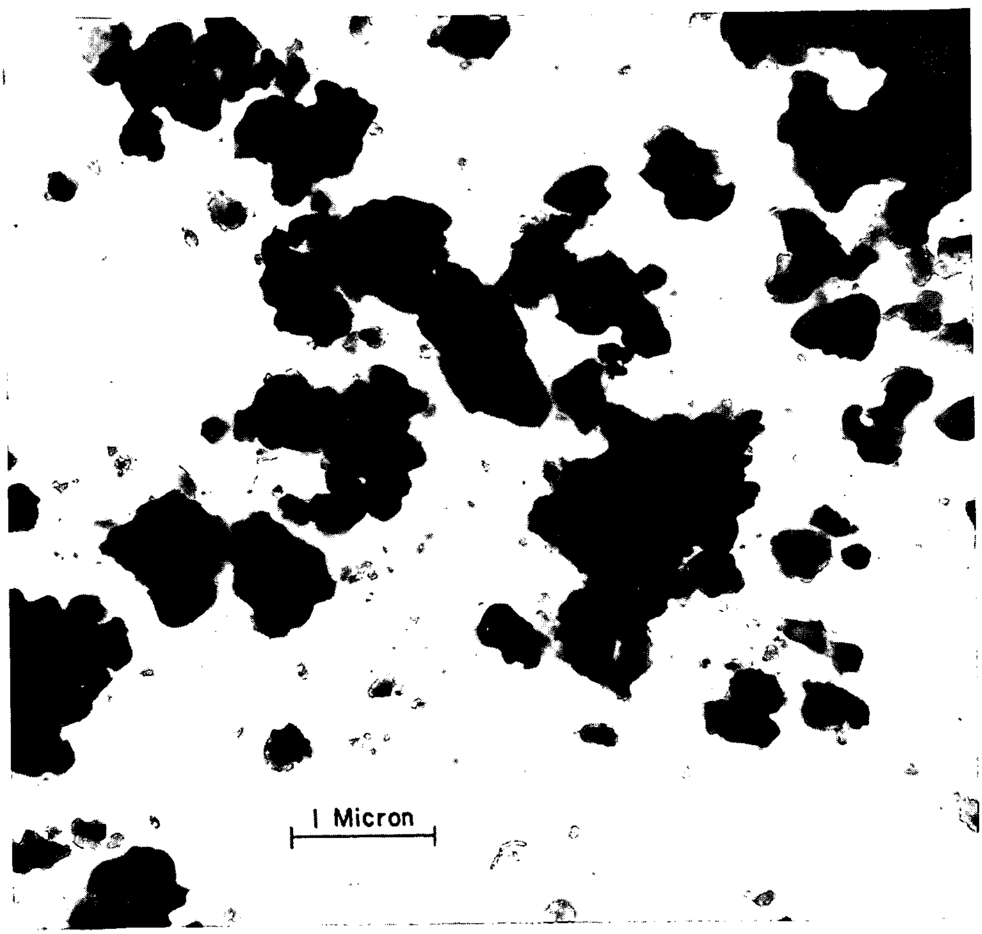

Plate 1

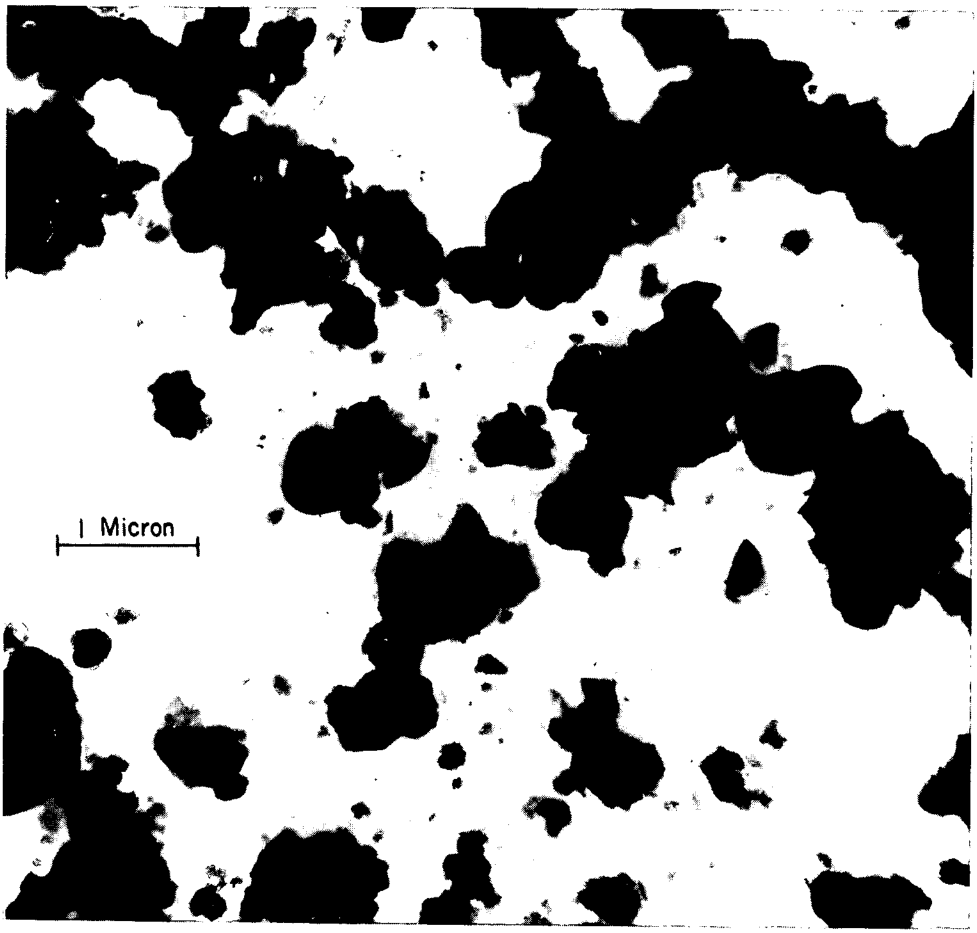

Plate 2